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14. ABSTRACT The fundamental activities involved use of various imaging techniques to study corrosion processes that occur at metal surfaces. We applied these methods to understand both the anodic and cathodic processes involved in corrosion at Al alloy surfaces, and how those processes are influenced by environmental conditions. The applied activities were development and testing of new corrosion inhibition systems based on blends of thermoplastics and conducting polymers. These blends contain smart controlled release polymers capable of releasing inhibitors in response to local pH changes. These unique materials combine the attractive mechanical properties of thermoplastics with the known corrosion inhibition properties of conducting polymers. Finally, we were involved in transfer of a novel chemical etching technology for Al alloy surface pretreatment to Luna Innovations, Inc. to produce new environmentally compliant coating systems for the protection of aging Air Force aircraft. Luna's technology is now being tested at AFRL laboratories.				
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# AFOSR Final Technical Report

## Objectives

This grant represents an effort comprised of both fundamental and applied activities designed to address corrosion concerns of pressing importance to DoD. The fundamental activities involved use of both existing and recently developed imaging techniques to study a variety of processes that occur at metal surfaces. We applied these methods to understand both the anodic and cathodic processes involved in corrosion at Al alloy surfaces, and how those processes are influenced by environmental conditions. An overall goal of this part of the project was to gain a quantitative understanding of the processes driving pit formation and stabilization so they can be reliably incorporated into engineering design metrics for corrosion systems. A second overall goal was to understand the time sequence of events in corrosion, so we can have better predictive capabilities for corrosive failure. The applied activities involved development and testing of new corrosion inhibition systems based on blends of thermoplastics and conducting polymers. These blends contain smart controlled release polymers capable of releasing inhibitors in response to local pH changes. These unique materials combine the attractive mechanical properties of thermoplastics with the known corrosion inhibition properties of conducting polymers. Various electrochemical and imaging methods were used to characterize the corrosion inhibition properties of the blend coatings. In addition, we pursued tests of a mechanism we have proposed that seeks to explain the way in which these blends inhibit corrosion. An overall goal of this part of the project was the development of new environmentally compliant coating systems for the protection of aging Air Force aircraft.

## Status of effort

We have made progress in several areas. First, we continued with the use of real-time fluorescence microscopy to indirectly image  $O_2$  reduction at the AA2024 surface. In this experiment, the  $OH^-$  generated by  $O_2$  reduction is used to produce the emissive form of a fluorophore. Through a variety of processes, the fluorophore production is limited to the region near the IP, allowing us to indirectly image  $O_2$  reduction at the IP's in real-time with sub-micron resolution. Second, wall-jet flow cell, rotating disk electrode (RDE) and scanning electrochemical microscopy (SECM) experiments have been used to study dioxygen reduction at IP's and how it is influenced by chromate treatment. This study has elucidated the manner in which chromate operates, and, importantly, showed that a surface previously damaged by dioxygen reduction is not as well protected by chromate as is a pristine, undamaged surface. Third, we completed a study of the protective action of a conductive polymer coating comprised of a poly(aniline) blend with poly(methylmethacrylate). We found that the coating protects the Al alloy by poisoning its potential in a region where  $O_2$  reduction is kinetically inhibited.

## Accomplishments/New Findings

We succeeded in using fluorescence microscopy to indirectly image  $O_2$  reduction at individual IP's in real-time. In this experiment, the  $OH^-$  generated by  $O_2$  reduction is used to produce the emissive form of fluorescein. Through a variety of processes (including use of buffers and photobleaching), the fluorophore production is limited to the region near the IP. This experiment gives a real-time fluorescence intensity signal that is directly proportional to the current for  $O_2$  reduction at individual IP's. We have observed several very interesting features in these images. First, we see some large, very bright IP's that seem to be continuously generating  $OH^-$ . Second, we see some medium sized IP's whose fluorescence intensity is highly variable on a timescale of a few seconds. Third, we see some very small objects (we are not certain if these are IP's or defects in the oxide layer) that literally flash on and off. This is the first real-time information of this type ever available, and we expect it to be critical in understanding how individual IP's of differing composition (such as  $Al_6(Fe, Cu, Mn)$  and  $Al_2Cu$ ) respond to treatments designed to inhibit  $O_2$  reduction. It may also be useful in providing the basic science for new approaches to monitoring for corrosion failure. A link from our web page (<http://uwadmnweb.uwyo.edu/chemistry/Faculty/Buttry/Surf4c.avi>) gives access to a video of fluorescence intensity versus time for dioxygen reduction experiments of this type that were done on a confocal laser scanning microscope in the UW Microscopy facility. The image in Figure 1 shows a single frame of that movie, in which the bright green objects correspond to IP's that are actively producing  $OH^-$  from  $O_2$  reduction. Because of the frame rates available from a variety of fluorescence microscopy techniques, it is possible to either watch this process in real-time (using a conventional fluorescence microscope) or to employ slower methods capable of sectioning the fluorescence intensity in the direction normal to the surface (using a confocal laser scanning microscope). Both approaches were actively pursued.



Figure 1



Various studies of dioxygen reduction at pristine and damaged (by dioxygen reduction) AA2024 surfaces were done using a wall-jet electrode flow cell, rotating disk electrodes (RDE) and SECM. We were especially interested in how chromate treatments influence dioxygen reduction at these two types of surfaces. The wall-jet experiments allowed us to easily switch between flow streams that are purged with either dinitrogen or dioxygen, while the RDE experiments give a simple way to quantitatively the  $O_2$  reactivity under different conditions. Both provide a fast and relatively straightforward assay of the total reactivity of the surface toward dioxygen reduction. SECM allows us to directly image cathodic activity on the surface. A significant finding was that chromate treatment **does not** protect AA2024 surfaces that have been damaged previously by dioxygen reduction. The figure above shows the initial deposition of a passivating layer of Cr(III) oxyhydroxide. As shown in Figure 2, the burst of cathodic current when chromate is added to a RDE cell shows that Cr(III) deposition occurs. Quantitation of the reductive charge shows that deposition occurs predominantly on the IP surfaces when the sample is pristine AA2024. After this, wall-jet and RDE experiments showed that

dioxygen reduction is essentially completely inhibited. SECM experiments confirm that cathodic activity has ceased on such a surface. In contrast, when the surface has been previously damaged by prolonged (or even short) dioxygen reduction, the charge for chromate reduction at the damaged surface suggests chromate reduction occurs everywhere (even on the Al-rich matrix surface). Further, this "treated" surface is not effectively passivated toward dioxygen reduction. Thus, chromate treatments are not very effective at surfaces that have already experienced surface damage due to the pH increase that occurs during dioxygen reduction. This may have impact on how such treatments are used in maintenance activities.

Finally, we explored the protective mechanisms for conducting polymer blends of poly(aniline) and poly(methylmethacrylate). In these experiments, we used open circuit measurements and SECM to monitor the behavior of an AA2024 sample coated with a thin film of the blend and then intentionally damaged it by scratching. We found that the blend poises the open circuit potential at a value sufficiently positive so that  $O_2$  reduction cannot occur at significant rates. In contrast, during the PMMA control experiment, the OCP drifts rapidly negative after the scratch, producing conditions where both  $O_2$  and

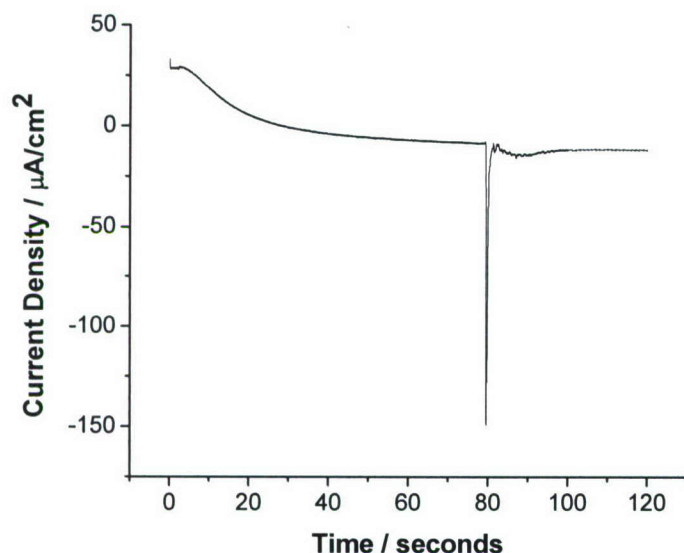


Figure 2

solvent (water) can be reduced. This produces  $OH^-$  and ultimately leads to the type of damage shown in a previous publication (#1 below). We are proceeding with additional experiments in this area.

We also developed a new multiple dip coat corrosion protection coating for AA2024-T3 based on alternate exposure to zirconium nitrate and octadecyl phosphonic acid. This is a simple dip coating procedure that can be done in under an hour. The best coating initially suppresses dioxygen reduction at AA2024 by two orders of magnitude, from  $0.3 \text{ mA cm}^{-2}$  to  $3 \text{ } \mu\text{A cm}^{-2}$ . After 2 hours the dioxygen reduction current is still suppressed by a factor of 20. We have characterized the coatings using advancing contact angle, glancing angle FTIR, scanning Auger and electrochemical measurements.

We also worked closely with Luna Innovations, Inc. on the application of a novel chemical etching technology we developed that removes intermetallic particles from the surface of AA2024. This has the potential to become a fieldable pretreatment that would be environmentally compliant. Luna has worked through a Phase 1 and Phase 2 funding period, and the technology is now being tested at the Coatings lab at Wright Patterson.

### Personnel Supported

Graduate students supported: Dr. Jesse Seegmiller (just graduated, now at Michigan State Univ.), Dr. Eric Dufek (now a postdoc at Univ of Utah), Tom Dziedzic (still in graduate school)

Postdoctoral fellow supported: Dr. Reinaldo Bazito

Collaborators: Profs. Roberto and Susana Torresi at the University of São Paulo, Brazil

### Publications

1. "Visualization of Cathode Activity for Fe-Rich and Cu-Rich Intermetallic Particles via Cathodic Corrosion from Dioxygen Reduction at Aluminum Alloy 2024-T3", Seegmiller, J. C.; Bazito, R. C.; Buttry, D. A., *Electrochem. Solid-State Lett.* **2004**, 7(1), B1-B4.
2. Adsorption of polyphosphonates on native aluminum oxide, R. C. Bazito; D. A. Buttry, *Proc. - Electrochem. Soc.*, 2003-25, 241 (2004).
3. Influence of local redox activity at Al alloys on corrosion, J. C. Seegmiller; R. C. Bazito; D. A. Buttry, *Proc. - Electrochem. Soc.*, 2003-23, 29 (2004).
4. "Mechanism of Action of a Corrosion Protection Coating for AA2024-T3 Based on a Poly(aniline)-Poly(methylmethacrylate) Blend", Jesse C. Seegmiller, José E. Pereira da Silva, Daniel A. Buttry, Susana I. Córdoba de Torresi, and Roberto M. Torresi, *J. Electrochem. Soc.*, **2005**, 150(6), B45-B53.

5. "Inhibition of O<sub>2</sub> reduction on intermetallic particles at the surface of AA2024 by adsorbed phosphonates", Bazito, Reinaldo C.; Seegmiller, Jesse; Buttry, Daniel A.. . *Corrosion Reviews*, **2007**, 25(5-6), 545-554.
6. "Dioxygen Reduction Affects Surface Oxide Growth and Dissolution on AA2024-T3", Eric J. Dufek, Jesse C. Seegmiller, Reinaldo C. Bazito and Daniel A. Buttry, *J. Electrochem. Soc.*, **2007**, 154 (9) C458-C464.

### **Interactions/Transitions**

1. *Participation/presentations at meetings, conferences, seminars, etc.*
  - a. "Inhibition of O<sub>2</sub> Reduction on Intermetallic Particles at the Surface of AA2024 by Adsorbed Phosphonates," Reinaldo C. Bazito, Jesse Seegmiller and Daniel A. Buttry, presentation at the First World Congress on Corrosion in the Military: Cost Reduction Strategies; Sorrento, Italy, June 2005.
  - b. "Adsorption of polyphosphonates on native aluminum oxide" Bazito, Reinaldo C.; Buttry, Daniel A., presentation at the 2003 Fall meeting of the Electrochemical Society, Orlando, FL.
  - c. "SECM Studies of Corrosion Protection Coatings on Al Alloys" J. Seegmiller, J. Pereira da Silva, D. Buttry, S. Cordoba de Torresi, and R. Torresi, Abstract #843, presentation at the 2003 Fall meeting of the Electrochemical Society, San Antonio, TX.
2. *Consultative and advisory functions to other laboratories and agencies, especially Air Force and other DoD laboratories.* We worked with a small company in Charlottesville, Virginia called Luna Innovations, Inc. They have had Phase 1 and Phase 2 SBIR funding for new corrosion protection pre-treatments based on chemical etching to remove IP's from AA2024 surfaces. This is a subject of a past AFOSR grant to our group. That technology is now being tested at the Coatings lab at Wright Patterson.
3. *Transitions.* Pending

**New discoveries, inventions, or patent disclosures.** NONE

### **Honors/Awards:**

- a) No recent honors during contract period
- b) Previous honors: Japan Society for the Promotion of Science Senior Research Fellowship, Visiting Professor at Caltech and University of Colorado, Editorial Advisory board for *Langmuir*, member of Board of Directors for Society of Electroanalytical Chemistry, Member at Large for Physical Electrochemistry Division of the Electrochemical Society.